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Prevention and Origin of Exceptional Deleterious Gas Compositions in Coal Mine

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Abstract

The abnormal content of gas compositions of H_2S, CO_2, CO and N_2 under coal mine has close relationship of safe production and comprehensive utilization of coal gas. According to original analyses of anomalous accumulation characteristics of the above-mentioned gas in China, the paper suggests that abnormal thermochemistry effect, osmosis effect of surface water, sealed effect of coalseam floor, coal types and coal metamorphose degree are the main factors which contribute to abnormity of deleterious gas compositions. Based on study of gas origin, primary measures for prevention and control of deleterious gas in coal excavating course were brought forward. The research has guiding significance for safe production of coal mine.

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Keywords: Coal gas; deleterious compositions abnormity; Origin; Comprehensive prevention

1. Introduction

A great deal of domestic and abroad studies show that coal gas is composed of methane, heavy hydrocarbon (such as ethane, propane, butane, isobutane), carbon dioxide, nitrogen, hydrogen, sulfur dioxide, hydrogen sulfide, carbon monoxide and inert or rare gas (helium, neon, argon, krypton, xenon). In different coalfield, well field, mining area, sides of mining area, and coal seam coal gas content and composition have some difference. The harmful compositions mainly include H_2S, CO_2, CO, and N_2, etc. The concentration abnormity of harmful compositions is one of main causes causing frequent occurrence of accidents in coal mines. The content disproportion is largely related with coal formation and geologic condition variation and tectonic evolution. It not only endangers safe production in coal mines, but also affects further utilization of coal gas. The paper analyzed the content abnormity factors of harmful

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compositions based on harmful coal gas composition and geological properties, as well as preliminarily discussed prevention and cure methods for the abnormity to help preventing correlative accidents.

2. Origin of exceptional deleterious compositions in gas

The main composition in coal gas is methane, whose content is usually above 90%, and nitrogen or carbon dioxide comes second[1]. But various composition contents are different in different coal seams (or surrounding rocks) or coal mining, sometimes even existing in great difference. Especially, when the content of H_2S, CO_2, CO and N_2 exceeds the permissible value of the Security Rules for Coal Mine, they will bring serious harm to coal production.

2.1. Sulfureted Hydrogen（H_2S）

H_2S is virulent and flammable gas, which smells like a rotten egg. The least concentration of H_2S that human nose can detect is 0.2-0.3 ppm, and the odour becomes strong when its concentration reaches 20-30 ppm. If the concentration is between100 and 150 ppm, it would make the smell sense paralyzed [2]. H_2S mainly activates respiratory tract and eyes of human body and high H_2S concentration can cause people suddenly poisoned death. Besides these toxicities, H_2S can produce anther poisonous gas, SO_2, after burning, and when it meeting spark it probably cause explosion with the concentration of 4.0-46.0% in air. H_2S is easily soluble in water at the rate of 2.6 Vol. gas/ Vol.H_2O at 20°C, 10^5Pa (table 1). In water or damp surrounding, H_2S shows acidity and has highly reactive and corrosive on all organic and metallic compounds. Therefore, for insuring the human body safety, the 105th of the Security Rules of Coal Mine prescribes the threshold limit concentration of H_2S is 6.6 ppm in mine airflow.

Table 1. The properties of several deleterious gas ingredients in mine [1]

Compound	Molecular formula	Dissolving quotiety in pure H_2O (20℃,10^5Pa)	Density of ideal gas ($kg \cdot m^{-3}$), 1atm,15.55℃	Relative density of gas (1atm, 15.55℃ air=1.0)	Threshold limit concentration in mine airflow (ppm)
Hydrogen sulfide	H_2S	2.580	1.438	1.177	6.6
Carbon Dioxide	CO_2	0.870	1.858	1.520	24.0
Carbon Monoxide	CO	0.035	1.250	0.967	5.0
Nitrogen	N_2	0.016	1.182	0.967	2.5

Origin of hydrogen sulfide in the nature can be divided into 3 types: Thermochemistry effect (include Thermochemistry Decomposition and Sulphate Thermochemistry Reduction), Biochemistry effect (include Biodegradation and Microbe Sulphate Reduction) and Magma effect [3].Among them, thermochemistry and biochemistry effect belongs to organic origin and magma effect belongs to inorganic origin.

1)Thermochemistry effect: While Sulphate contacts gaseous hydrocarbon in coal bearing, Oxidation-reduction may be taken place [4]. That is, Sulphate is deoxidized, and hydrocarbon is oxidized, and hydrogen sulfide is produced, namely:

$$\sum CH + CaSO_4 \rightarrow CaCO_3 \downarrow + H_2S \uparrow + H_2O \qquad (1)$$

At this course, another reaction of producing H_2S is organic carbon to react with sulphate in coal bearing strata, namely:

$$2C + CaSO_4 + H_2O \rightarrow CaCO_3 \downarrow + H_2S \uparrow + CO_2 \uparrow \qquad (2)$$

In coal bearing strata, most H_2S produced by thermochemistry decomposition and sulphate thermochemistry reduction is escaped during the uplifting of coal measure strata or the groundwater seepage flow process. But hydrogen sulfide formed by magma thermodynamic in the late stage, which is occurred in the coal seam easily cause exceptional concentration, such as Bayi colliery in ZaoZhuang, CuiZhuang colliery in WeiShan county of ShanDong Province.

2) Biochemistry effect: The original hydrogen sulfide is formed by biodegradation and microbe sulphate reduction effect belonging to the biologic gas that can only existed in peat-brown coal stage [5]. During the course of late structural evolvement, coal-bearing strata was uplifted, and the secondary hydrogen sulfide would be probably formed by microbe sulphate reduction under the process of groundwater in lower or middle coal rank areas. The equation of the biochemistry function can be expressed as follow:

$$\sum CH[orC] + CaSO_4 \xrightarrow{\text{sulfate reducting bacteria}} CaCO_3 + H_2S \uparrow + H_2O \quad (3)$$

3) Magma effect: The sulfur element abundance in the earth interior is far higher than that in the crust. The magma activities make deep rocks melt-out and form volatile components containing hydrogen sulfide, so the volcano eruption matters usually contain hydrogen sulfide. This kind of hydrogen sulfide's content is very unsteady in coalbearing strata, because it depends on the composition of magma that intrudes coal series, gas migration conditions and so on. But under the given migration and accumulation conditions, it also can cause the abnormal content of hydrogen sulfide in coal mine.

The current researches show that origin of H_2S in mine gas is mostly organic or thermochemistry effect. H_2S produced by biochemistry and secondary biochemistry effect (produced by microbe reduction from the groundwater after the stage of diagenesis, low or middle coal rank) mainly appeares in low or middle rank coal [6].

2.2. Carbon Dioxide（CO_2）

Carbon dioxide is a colorless, odorless and sourish gas. At 1 atmospheric pressure, 15.55℃, its density is 1.858kg/m^3 with relative density of 1.520. CO_2 can be solved in water at the rate of 0.9 Vol. gas/ Vol. H_2O at 20°C, 10^5Pa (table 1). Its outburst can causes body suffocated.

The origin of carbon dioxide adsorbed in coal seam can be divided into three types: groundwater osmosis, Magma effect, and structural stress sealing effect.

1) Groundwater osmosis: When surface water with certain concentration carbon dioxide penetrates into coal bearing strata, carbon dioxide is strongly adsorbed by coal.

2) Magma effect: Since Mesozoic, magmatic activity occurred so intense in our country that many coalfields and mining areas were influenced. Therefore, most origin of outburst of coal and carbon dioxide is inorganic [7]. That's means, thermal magma coming from deep strata contains a great deal of volatile FeF_3. Carbon dioxide is produced when FeF_3 contacts with limestone ($CaCO_3$).

$$2FeF_3 + 3CaCO_3 \rightarrow Fe_2O_3 + 3CaF_2 + 3CO_2 \uparrow \quad (4)$$

If limestone contains silica, the reaction will be:

$$2FeF_3 + 3SiO_2 + 6CaCO_3 \rightarrow Ca_3Fe_2Si_3O_{12}(Garnet) + 3CaF_2 + 6CO_2 \uparrow \quad (5)$$

In magmatic intrusion area where thermal metamorphism of coal is intensified, permeability of roof and floor of coal seam is increased, and new generative carbon dioxide is easy to be adsorbed by coal seam. Moreover, carbon dioxide desorption velocity exceeds that of methane. If gas contains a great deal of carbon dioxide, the pressure gradient will increase, so outburst intenseness will be more violent than methane. The outburst accidents of south wing mining district of Zhangergou colliery in Lanzhou in Gansu province, Songxiaping colliery in Shanxi province and the No. 5 colliery of Yingcheng colliery in Jilin province are all belong to this kind [8-9].

3) Structural stress seal effect: The study on carbon dioxide outburst happened in Yaojie coalming of Gansu province showed coal seams occured pyrolysis under magmatism, and then a great deal of carbon dioxide gas was produced whose accumulation was controlled by the turbo shape faults lying on the constringent end of the brush structure and the strong stress field, and was sealed by stress of fault zone.

These factors resulted in carbon dioxide storage in thick coal seam [10-11].

2.3. Carbon Monoxide（CO）

Carbon monoxide is a colorless, odorless, highly poisonous and flammable gas. CO solubility is very low, at the rate of 3.5 Vol. gas/ 100 Vol. H_2O at 20°C and 1 atmospheric pressure. The density of CO is 1.250kg/m^3 with relative density 0.967 (table 1). Combining with hemoglobin velocity is quicker than that of oxygen, which could stop body cell metabolism soon because the hemoglobin can't take oxygen any more, and then cause body's cell anoxia. If body exposes in a low concentration of carbon monoxide for a long time, man will get headache, vomit and other inconspicuous or hard cure symptoms, and staying in high concentration for only several seconds, man will be asphyxiation and stupor.

In coal mine, the origin of exceptional carbon monoxide concentration mainly include the followings:

1) Magmatism: After high temperature magma intruding into coal bearing strata, the organic carbon in coal occurs an incomplete oxidization in oxygen shortage, and then a great deal of carbon monoxide is produced, namely:

$$C + O_2 \xrightarrow[\triangle]{} CO \uparrow \tag{6}$$

2) Spontaneous combustion effect of coal seam: Some coal with low burning point slowly burns in the weathered or oxidized zone and well-ventilated condition of mine after theirs critical temperature arrives the burning point. It is easy to cause exception of CO in poor-ventilated condition of mine and fire area, for example, Liu Huanggou colliery in Xinjiang autonomous region.

2.4. Nitrogen（N_2）

Nitrogen is a colorless, odorless gas. It can dissolve slightly in the water. N_2 is only soluble in water at the rate of 0.016 Vol. gas/ Vol. H_2O at 20°C and 1 atmosphere, its density is 1.182kg/m^3, and relative density is 0.967 (table 1). If the concentration of nitrogen in mine is too high, the sub-pressure of breathing oxygen will declines, which will make person asphyxia for lack oxygen.

Nitrogen occurred in coal seam derive mainly from weathered or oxidized effect, groundwater penetration and oxygenation of roof red layer with ammonia in coal.

1) Weathered or oxidized effect: When coal seam has an outcrop, coal gas will migrate from deep to shallow. At the same time, air with some nitrogen permeates or diffuses towards coal seam along outcrop.

2) Groundwater penetration: During the course of coal metamorphism, water carrying with O_2, CO_2 and N_2 penetrates into coal bearing strata, gets in touch with coal seam extensively, and then O_2, CO_2 is consumed by metamorphism, and N_2 is kept down. For example, TengNan colliery in Shandong Province [12].

3) Oxygenation of red beds with ammonia in coal: a lot of methane and ammonia produced in the course of coalification meet with Fe_2O_3 of the overlying red beds, ammonia is oxidized into nitrogen by Fe^{3+} ion, and nitrogen occurred in the coal seam and the surrounding rock.

$$2NH_3 + 3Fe_2O_3 + 3H_2O \rightarrow 6Fe(OH)_2 + N_2 \uparrow \tag{7}$$

This effect that cause exceptional nitrogen content in coal seam needs three conditions: 1) There is plenty of coalforming plant with abundant N element, which is the foundation of producing a great deal of ammonia; 2) Coal seam must be covered by red layer, ammonia can be oxidized into nitrogen, or else ammonia will be taken away by groundwater because of its easy solubleness; 3) Coal has strong adsorbed capacity on nitrogen, while the red beds are covered by gasproof or poor permeability rocks, it leads to exceptional nitrogen concentration, such as Liuqiao colliery in HuaiBei, Chacheng colliery in XuZhou and Chaili collieries in Zaozhuang[13].

3. Prevent and Control Measures

The occurrence states of coal gas mainly include adsorbing gas (quasi-liquid state), dissolving gas and free gas in coal mine, and maybe exist absorbing gas(solid-liquid solution). But these states may convert mutually, and lay a dynamic equilibrium in the conditions of original temperature and pressure. Coal adsorbability increases with the gas's boiling point [6].When the coal resource bear mined, adsorbing gas will desorbs to free gas continuously and dissolving gas also releases from water as the coal seam pressure decrease. Therefore, predicting and curing methods should be adopted in the light of physical and chemistry property, state and concentration of gas in coal.

1)Drainage: A method of pumping gas, that is, gas which is drained from drilled borehole in coal bearing strata is piped by differential pressure. This method belongs to physical one which can be applied to cure various harmful gases such as H_2S, CO_2, CO, and N_2, especially in high concentration condition. The methods include in seam gas drainage, adjacent layer and frommined area drainage. To current-seam, drainage methods may be adopted like through-layers drilling, the horizontal drilling, the cross drilling, through-seam gridding drilling, the unsplited blasting of deep drilling hole, the hydraulic slotted liner, the hydraulic fracturing, and the hydraulic reaming. To adjacent layers, drainage methods may be adopted as layers drilling hole through roof (or floor), rock drift and long horizontal drilling hole in roof. Coal mine goaf drainage can be adopted the methods of the caving zone drilling hole, the buried tubes.

2) Infusing: An infusing method is that infusing chemical absorbent neutralizes the deleterious ingredient of gas (belonging to chemical process). This has better effect on curing of acidic H_2S, CO_2 and also can be applied for other high solubility ingredients. The experimentation of infusing alkaline liquor to the gas drainage hole showed that the discharge quantity of H_2S can be reduced between 50 to 70 percent [14]. In the selective experiment of absorbent for reducing H_2S in coal showed the effect of buffer solution is better than water [14].

3) Spraying: A spraying method. In the course of blasting mining or mechanical mining, by spraying alkaline liquor, adopting hydraulic mining, or using liquid absorbent to neutralize the deleterious ingredient of gas in terms of their characteristics after coal falling, effective cure can be obtained. These methods are mainly fit for easily resolvable ingredient like anomalous H_2S and CO_2. To exceptional CO and N_2 content, oxidant should be used firstly in order to translate them into acid gas, and then neutralization methods can be adopted.

4) Covering: A method of covering foam, that is, the releasing gas will be covered or adsorbed by spraying float containing sorbent to cutting parts of drum of coal cutter and coal conveyor belt to make the rolling coal covered by float to reduce airflow quantity of deleterious ingredients of gas. This method, which mainly makes use of the difference of solubility of deleterious ingredients in different solvent, is usually used to adsorbing gas and free gas of fine coal with lower concentration. It is fit to exceptional H_2S and CO_2.

5) Dilution: A method (physical method) of ventilation in coal mine, that is, concentration of deleterious ingredient will be decreased by adding other harmless ingredient (such as air, oxygen) rate. The concentration of deleterious ingredient can be insured below the permitted value by the calculation of air volume. The ventilation way is the last line of defence to cure gas, and can be applied to exception of H_2S, CO_2, CO, and N_2.

Besides the common predicting measures, such as installing professional monitors, adopting pre drainage, setting independent ventilation, insuring air quantity in the course of mining, etc., we also should take different measures to alleviate or avoid disaster based on its origin and characteristics:

1) Special Geology Structure Zone: If coal seam is covered by the red layer, the concentration of N_2 of gas should be monitored. While magmatic rock had intruded into coalbearing strata, the concentration of CO_2 and H_2S should be monitored. While meeting structure coal or the high stress field, CO_2 should be monitored.

2) Groundwater active Zone: Because both of them are easily dissolving in water, the concentration of

H_2S and CO_2 should be monitored, and the amount of spraying water in course of blasting or machine mining should be increase. Once meeting temporally accidents of H_2S and CO_2, the removing workers can use wet towel to avoid poison.

3) Different deleterious ingredients: While meeting the concentration of H_2S and CO_2 abnormal content, the measures should be adopted for miner to remove to the intake along the higher part. Because the concentration of these kinds gas is higher than air, lower hypsography and the lee are more dangerous. While meeting the odorant like the rotten egg of H_2S or the sourish of CO_2, worker should remove immediately. To the coal with low burning point, the flameproof explorer should be adopted.

4. Conclusions

In China, the contribution factors of abnormal content origin of H_2S, CO_2, CO and N_2 in coal mine gas mainly have the follows:

1)Abnormal Thermochemistry Effect: In the later stage of primary coalification, under the certain pressure, the high temperature caused by magma or tectonic action will push the reaction toward the direction of producing H_2S, CO_2 and CO, which will accumulate in the coal seam for absorption of coal that lead the exception of concentration.

2) Surface water's permeation effect: The diffluent gas taken into coalbearing strata by water, will separate from the water with transform of pressure and temperature, and be absorbed largely by coal for coal has strong absorption capacity to H_2S and CO_2, which will cause their anomalous phenomena.

3)Sealing effect of the roof of coal: While the coal seam is covered by the rock layer of gasproof or poor permeability, poisonous gas separating from the water or new producing from chemical reaction will be assembled and lead exception.

4) Degree of coal metamorphism: coal rank controls the production of biologic gas or secondary biologic gas, and determines the burning point of coal. So, it is one of the important origins of exceptions.

To cure the exceptional deleterious components in gas, we ought to adopt not only the corresponding predictions and monitor measures, but also particular measures aiming at its physical or chemical characteristics under the principle of drainage, infusing, spraying, covering and dilution.

While the concentration of deleterious gas is very high, pre drainage should be adopted in mine firstly to transport them to the ground, and then cure it by physical or chemical method. While the concentration of abnormal gas is lower, spraying and covering are major methods suggested to apply to in mine.

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